Weaponization and Characterization of Nanoenergetics

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DISCLAIMER

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Nanoenergetic ingredients, from carbon nanotubes and nanoaluminum to nanoparticles of explosives and oxidizers, are being investigated for incorporation in novel formulations for weaponization applications. Advanced characterization technologies such as LIBS (Laser Induced Breakdown Spectroscopy) & the high-resolution electron microscopes at the NCEM (National Center for Electron Microscopy) can provide powerful clues for advancement in the science of nanoenergetics.

The central or clue component of modern weapon systems is the energetic material either in the form of an explosive or a propellant. The research in novel energetic materials and their weaponization is at the heart of defense. Out of this research a new class of materials has recently emerged known as "nanoenergetics". One of the goals pursued is to arrive at new, more insensitive, energetic materials with improved performance properties for application in weapons or munitions, providing optimum deployment accuracy and strategic effectiveness and thus human safety, a prime concern. Nanomaterials, or nanoenergetics, can be used to improve various components of weapons or munitions such as the ignition and propulsion, as well as the warhead part of the weapon (*1*). In the latter application, nanoenergetics hold promise as useful ingredients for the thermobaric (TBX) and TBX-like weapons, particularly due to their high degree of tailorability with regards to energy release and impulse management (*1*).

Recent groundbreaking advances in the development of novel nano-scale materials and technologies, have shown the potential to radically improve the safety and performance properties of propellant formulations. One of the major emerging technologies in the field of nano-materials is that of the carbon nano-tube. These long thin cylinders of carbon, consisting of graphitic single-atom layers "rolled" up into cylinders, were first discovered in 1991 by S. Iijima (*2*) using high-resolution electron microscopy. The cylinders are typically tens of nanometers in diameter and several microns in length. The unique coiled graphitic structure confers remarkable properties on the carbon nano-tubes. Thus, the longitudinal strength is reported (*3*) to be up to one hundred times that of steel! The carbon nano-tubes possess a very high electrical conductivity along their lengths reaching stable current densities (*4*) of up to 10^{13} A/cm^2 which corresponds to 120 billion to 3 trillion electrons per second! (a typical 18-gauge copper wire carries a current density of up to 10^2 A/cm^2) and the thermal conductivity is extremely high, approaching that of diamond (*5*), the material with one of the highest reported thermal conductivities. The properties of carbon nano-tubes clearly set them apart as a new candidate ingredient for energetic formulations with the potential of improving the properties of the same without adding any adverse environmental effects.

Finally novel energetic materials offer the promise of much higher energy densities and explosive yields in comparison to conventional explosives (*6*). Explosives and propellants have been in existence for many years prior to the discovery of dynamite by Nobel in 1867. However the initiation, sensitivity and safety aspects of explosives and some of the fundamental notions utilized by chemists in the synthesis of new energetic molecules are still to date primarily empirical. With the advent of new technologies for nanoscale characterization, major advances in our understanding of the atomistic/ molecular behavior of energetic materials are under way. This fundamental knowledge-basis is of assistance in the development of improved novel energetic materials and nanoenergetics for application in defensive weapons with increased effectiveness in their important mission to save human life.

Functionalized Carbon Nanotubes for Nanoenergetic Applications

Carbon nanotube (CNT) incorporation in propellant formulations offers the potential for burning rate and combustion tailoring due to the very high thermal conductivity of the CNTs. Furthermore the exceptionally high electrical conductivity of CNTs may be exploited for the improvement of propellant initiation for either an advanced plasma-based initiator (which is under development), or for use with more conventional electrical initiators. Finally the mechanical properties of the CNTs may be reflected in improved mechanical properties for the formulation as a whole. Research is being pursued to derivatize these compounds for incorporation in propellant mixes, ultimately with energetic functional groups that would improve performance and facilitate dispersion into a polymer matrix.

Figure 1 shows an electron micrograph of PEI (polyethyleneimine)-modified carbon nanotubes with a magnification of 40,000x. As can be seen from the micrograph, the tubes appear distinct with a clear center core and a 'thick' outer wall consisting of six to nine graphitic layers. The lengths of the tubes are on the order of 20 μm, while the average diameter is approximately 20 nm. Clear surface features or defects occurring at regular intervals of about 20-60 nm are evidenced in this "bamboo" CNT morphology since the functional groups have attached at the "bamboo" defect sites. These defect areas consist of terminated carbon bonds with COOH groups as shown in Figure 2 where the functional groups are attached by chemical titration.
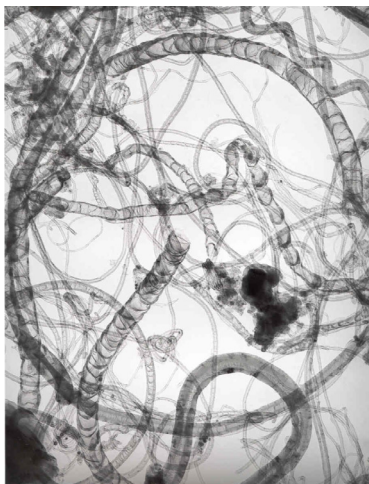
Figure 1. High-resolution transmission electron micrograph of polyethyleneimine-modified carbon nanotube (40,000 x)

D-GC-MS (Desorption Gas Chromatography-Mass Spectroscopy) results for the virgin CNT samples showed no indication of organic solvent present, consistent with the fact that these materials are produced under conditions of high temperature and pressure with metal catalysts. The D-GC-MS analysis of the polyethylenimine-modified (PEI) and poly(methylmethacrylate) (PMMA)polymeric samples was also performed on the nanotubes before and after vacuum exposure. The PEI samples desorbed with a 400 °C pulse yielded acetic acid. In addition, the non-vacuumed sample yielded species such as the THF solvent and 1,3-cyclohexadiene, and ethynlcyclobutane, which were not observed from the samples held under vacuum. Compared to the non-modified tubes, the PEI-modified tubes seem to be slightly resistant to thermal decomposition with the 400 °C pulse, particularly in the case of the vacuumed tubes. With the dual D-GC-MS 400/700 °C pulse treatment, the PEI-modified samples yielded larger fragments (multiple-ring compounds) than the unmodified nanotubes.

PMMA-treated samples had solvent levels that greatly exceeded either the PEI- or unmodified CNT samples. The levels diminished with vacuum treatment, but because the original level was so high, the solvent levels in the vacuumed PMMA samples remained far higher than those discussed above. The D-GC-MS experiments showed that the carbon nanotubes are quite thermally stable, and that decomposition can be very dependant on factors such as the occluded solvent level and the nature and extent of the modification. The affinity of carbon nanotubes for retaining solvents or species of interest will be further investigated. Such information may be important for assessing the chemical purity of the tubes and to assist in the design of the modified or derivatized carbon nanotubes.
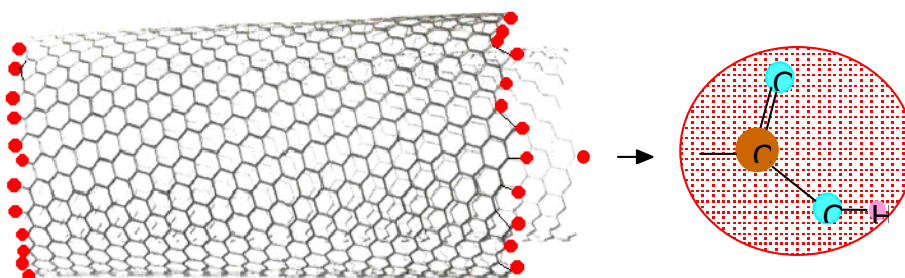

Figure 2. Carboxylic Defects in CNT "Bamboo" Structure.

Prompt gamma activation analysis (PGAA) by neutron scattering of the CNTs was performed at NIST and used to determine the C/H ratio, which was found to be 600:1. From known carbon-to-carbon bond distances and the fact that defect sites occur at regular intervals, the defect density was estimated from the PGAA data and compared with the electron microscopy measurements. The estimates indicated the presence of 5-membered or "squeezed" carbon rings amidst the 6-membered rings and different tube chiralities or "twists".

Novel techniques for incorporating "nano-energetic" particles into nanotubes are under investigation. The unique structure of carbon nano-tubes, may be used for confining the "nano-energetic" crystals in a nano-matrix with a positive effect on vulnerability properties. Thus, the possibility exists for simultaneously improving reactivity and stability of energetic materials, usually opposing characteristics. Figure 3 shows the concept for nanotube encapsulation of nanoenergetic particles.
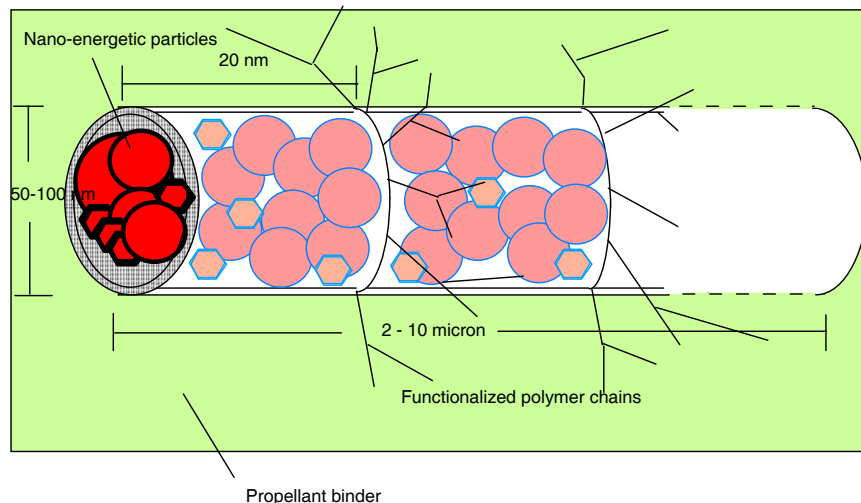
Figure 3. Concept for CNT encapsulation of nanoenergetic particles

Finally the development of a new nano-filter CNT technology with the potential for "filtration" or decontamination from air-borne bio-chemical warfare agents is under development.

Nanoenergetic Components of Propellants

The number and type of nano-energetic materials produced worldwide is increasing due to the potential impacts on future energetic formulations and other applications. Novel technologies for the production of new nano-scale materials are developing at a rapid pace. The incorporation of nano-energetic components in formulations, where the individual crystallite components are nanometric in size, such as oxidizers or fuels, has shown the potential to create or promote an extremely efficient and rapid degradation of propellants, leaving little or no un-reacted residue. This will also lead to environmentally clean or benign formulations. Furthermore the introduction of nano-energetic components may potentially improve the performance properties of propellant formulations by increasing on the control and rate of the localized "energetic" chemical reactions. A distribution homogenization of the "reaction centers" throughout the formulation, by the incorporation of nano-energetics, gives greater control of the overall burning by producing a smoother burning spread or reduced localized "hick-ups". Different architectures in which nano-scale energetic materials are embedded in energetic matrixes can thus be studied and designed with the added support of theoretical modeling at the molecular level. Typical nano-energetic ingredients, which are being investigated for incorporation in formulation mixes can be sub-divided into inorganic nano-fuels, nano-oxidizers and/or nano-explosives.

Nanoaluminum particles manufactured by NSWC-IH have been examined at a resolution of 1.6Å using the NCEM (National Center for Electron Microscopy) Atomic Resolution Microscope (ARM). With suitable specimen preparation, it will become possible to obtain images at even higher resolution using the OAM (One-Angstrom Microscope), a recent technological breakthrough at the NCEM Lawrence Berkeley National Laboratory (*7*). The OAM has achieved sub-Ångstrom resolutions down to 0.78Å and allowed for the first time the imaging of atoms of light elements such as carbon, nitrogen and oxygen, next to heavier metallic elements in solids (*8*). The OAM is to date the electron microscope with the world's highest resolution (*9*).

2.5 nm

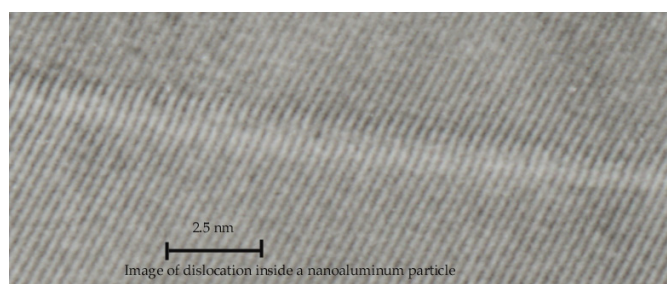Image of dislocation inside a nanoaluminum particle

Figure 4."Dislocation" inside aluminum nanoparticle

The high-voltage JEOL ARM-1000 microscope was used at an electron energy of 800 keV and a magnification of 600kX to ensure adequate electron beam penetration of the whole (non-sectioned) nano-aluminum particles. The images obtained from the ARM were laser scanned at the University of Maryland and examined with the computer by enlarging local areas of the micrographs. Figure 4 shows the image of a dislocation found inside a nanoaluminum particle.

There were typically 3 to 4 individual non-interacting dislocations per nano-aluminum particle within an otherwise perfect crystalline aluminum structure. Figure 5 shows two fused nanoaluminum particles. The grain boundary is evident together with the amorphous oxide coating at high resolution. Figure 6 shows the oxide coating, revealing the exfoliation of single molecular laminar sheets of aluminum oxide. The single "sheets" can contain tens of aluminum oxide molecules along their length. The smaller the size of the laminar sheets, the greater is the exfoliation. This could be a clue to reducing the barrier to reaction of the nanoaluminum particles when incorporated in a formulation as a nano-fuel.
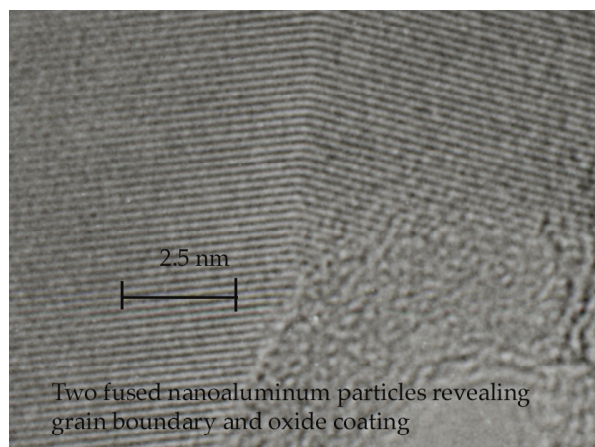
Figure 5. Two fused nanoaluminum particles

X-ray scattering measurements performed on the nanoaluminum indicate an amorphous coating of aluminum oxide. This is evidence for the fact that the areas of localized order, which are present in the laminar sheets, are very small or "nanoscopic". Furthermore impurities such as Fe, Cu and K (and N for the Russian ALEX) have been detected by x-ray photoelectron spectroscopy (*10*). This surface characterization technique and the high resolution electron micrographs are providing evidence for the fact that the impurities are localized within the oxide coating. Tailoring of the impurities may be used to facilitate or trigger the oxidation reactions of the nanofuel as well as potentially triggering other "energetic" reactions. In fact a new class of "nano-fuels" which may be imparting improved burning rate

characteristics to propellants is developing known as "mechanical alloys" (*11*). A "mechanical alloy" can be defined as a metastable metal-based compound where a phase change is induced in the material, which affects the ignition delay and combustion rate of the formulation. In order to produce the desired phase change rapidly, the materials are rendered metastable by using solid solutions of a base metal as solvent and another component either a metal or gas such as hydrogen, as a solute. In such metastable solid solutions, the rate of phase change of the material is not limited by diffusion in the condensed material. High-energy ball-milling under varying operating conditions has been used to synthesize "mechanical alloys" (*11*) in nanoparticle form such as Al-Mg, Al-Mg-H, B-Mg etc. where formation of the thermodynamically stable intermetallic phases was prevented during mechanical alloying by selecting appropriate process parameters.
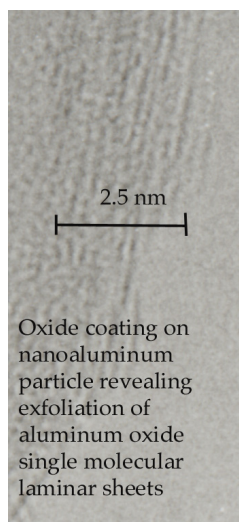

Figure 6. "Exfoliating" aluminum oxide coating

The technologies to produce "nano-oxidizers" and/ or "nano-explosives" are under development. Typical targeted compounds consist in PETN, RDX, HMX and HNS. The most common technique utilized is the RESS or Rapid Expansion of Supercritical Solutions. This technology is normally applied in the manufacture of nano-powders of inorganics and ceramics. It consists in the rapid expansion through a fine nozzle of a super-cooled solution of the energetic material in liquid super-critical carbon dioxide. This technique has been successfully applied by Dr. John Kramer at LANL to manufacture nano-sized particles of PETN. The LANL laboratory plans to utilize the same technology and set-up in the production of nano-sized HNS as well as up-scaling the production of PETN. Other Laboratories throughout the world are also developing techniques for the manufacture of nanosized explosives and oxidizers.

The National Center for Electron Microscopy

The National Center for Electron Microscopy is a DOE-funded Electron Beam Microcharacterization User Facility managed by the University of California.   The NCEM (http://ncem.lbl.gov/) was established in 1983 as a center for high-resolution transmission electron microscopy with the world's (then) highest resolution microscope, the Atomic Resolution Microscope (ARM), the first JEOL ARM-1000. The microscope has a resolution of 1.6Å and operates with electron beam energy of 800keV. This high energy allows the electron beam to penetrate and provide images of whole aluminum nanospheres up to several hundred Ångstroms in diameter.

Greater resolution (to 0.8Å) is provided by the One Ångstrom Microscope (*7*), a Philips CM300FEG/UT that has been specially aberration corrected and modified to improve its information transfer limit. This microscope can produce a focal series of images containing mixed-phase information that is computer processed to produce a single image to 0.8Å resolution, with all image phases corrected so as to faithfully display atom positions.   This microscope has been able to produce images (*8*) showing both the Al and O atom columns in sapphire (Al_2O_3). Because the OÅM operates with a lower beam energy (300keV) and at higher resolution than the ARM, specimens must be specially prepared to be less than 100Å thick in order to achieve the available sub-Ångstrom resolution.

To prepare specimens to the requisite thickness for the OÅM, the NCEM operates a specimen preparation facility equipped with a specialized ion-beam thinner (South Bay IV3 ion mill with low voltage ion gun) that can produce the relatively-large very-thin areas of sample required to take advantage of the best-available resolution of the OÅM. Less-precise ion-beam thinners are used to prepare samples for insertion into the IV3 for the final thinning step. In addition, a full range of sample machining tools is available, including a dual-beam FIB from FEI.

Microanalytical characterization is available at the 1nm (10Å) level with a Philips CM200FEG/UT equipped with a Gatan Image Filter (GIF) for Electron Energy Loss Spectroscopy (EELS) and EmiSpec software for spectrum analysis. Improved micro-analytical spatial resolution (down to 2Å) will become available when a Philips Tecnai 20 is brought on line in 2003.

Atomic/ Molecular Fundamentals of Energetic Materials

Nanoscale research studies have revealed that the start or nucleus of a chemical reaction in energetic materials is localized at the nanometer scale and forms inhomogeneously on the surface of the material (*12*). The energetic material can thus in itself be categorized in the class of nanomaterials. As an example, the initiation of ammonium perchlorate was investigated with various nano-imaging technologies together with chemical analytical tools. It was found that reaction always starts in localized sites generally termed in the literature as "reaction sites". These sites appear to follow the shape or crystallography of the material on which they form and expand in a non-homogeneous manner to consume the whole material. The "reaction sites" are typically of the order of 20-50 nm and smaller which tends towards the atomic/ molecular dimensions.

The sensitivity to initiation of different crystalline polymorphic forms of the same energetic material is known to differ. Similarly single crystals of energetic materials such as PETN (penta-erythrotritol tetranitrate) and nitromethane show a shock initiation sensitivity anisotropy (*13*). The crystal structure of the energetic materials is thus known to control the initiation sensitivity of the same. How the crystal structure affects the initiation has been studied experimentally and theoretically (*14*). It was found that the orientation of the molecules surrounding a given molecule in the crystal lattice appears to influence the initial decomposition reaction of the molecule.

This can be understood for example by comparing the crystal structure of the different polymorphs of HMX (cyclotetramethylene tetranitramine). As can be seen from Figure 7, the delta polymorph crystal structure is configured such that six out of eight of its oxygen atoms are positioned relative to the surrounding hydrogen atoms in an optimum position to form water molecules, one of the main reaction products of explosives and only two out of eight atoms in the alpha polymorph are in such favorable positions (*14*). Delta in fact is the most sensitive polymorph to initiation.

Such experimental observations and theoretical analysis are providing support for the fact that although different physical mechanisms may be occurring during the process of thermal, impact and shock initiation, one constant binds them all and that is the atomic closeness of the oxidizable and reducable elements of neighboring molecules in the crystal lattice of the material. This appears to promote the possibility of the co-participation of neighboring molecules in a localized concerted reaction which is triggered when the two molecules approach close enough at a single point to start reacting. The

nucleus for chemical reaction is thus nanoscopic in dimension. Further evidence comes from early work where the size of the smallest decomposition nucleus was being estimated (*15*). Thus experimentally (*16*) it was found that when rapidly moving atomic and nuclear projectiles are "fired" onto a lead azide surface, detonation occurs except when alpha-particles or electrons are used as projectiles. Alpha-particles and electrons have the smallest cross-section and would only activate a single molecule of lead azide. When ions of argon and mercury were used, which are large enough to activate neighboring molecules, explosion takes place. This supports the fact that two neighboring molecules are necessary for the formation of the first "reaction site". This physio-chemical effect has been termed "metastable trigger intermolecular initiation mechanism".
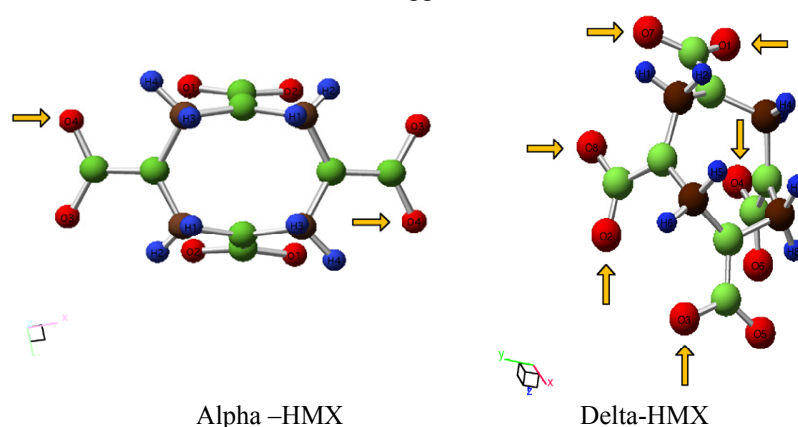

Alpha –HMX   Delta-HMX

Figure 7. Alpha and delta polymorphs of HMX (cyclotetramethylene tetranitramine).

Standard Arrhenius kinetic analysis indicates that in the thermal decomposition of energetic materials the explosive reaction occurs as a result of the breaking of the first bond, say the C-N bond in the explosive molecule. However in the Arrhenius kinetic analysis a transitional excited state of the molecule, of which not much was known was assumed prior to bond breaking. Since the transitional excited state is very short-lived, it can only be analyzed with the most advanced techniques of high-resolution temporal laser spectroscopy. Dr. A. Zewail, 1999 Nobel prize for chemistry for the development of femtosecond laser spectroscopy, studied the combustion reaction between hydrogen and carbon dioxide in the atmosphere. He found that the reaction,

$$H + CO_2 \rightarrow CO + OH$$
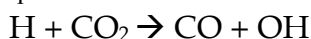
crosses a relatively long transitional state of HOCO (1000 fs). The transitional excited state incorporates a bonding oxidation-reduction reaction, which is followed by bond rupture only 1000 fs later.

An oxidation-reduction reaction requires the re-arrangement of the electrons in the orbitals and is thus fundamentally electronic. This agrees with the band gap observations by B. Kunz and the detonation velocities of energetic materials. The beauty in the crystals of solid explosives is that the 3-D arrangement and repetition of atoms is "frozen" in space and reactions start to occur in the solid phase. Thus different arrangements provide for more or less favorable oxidation-reduction reactions and can be handled by 3-D atomic/molecular predictive codes, which are being developed for the purposes. Such tools can provide additional data for the chemical synthesizers to target and tailor novel energetic materials with improved properties.

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